

Improved process for the singlet oxygen oxidation of organic substrates

5 The invention relates to an improved process for the singlet oxygen oxidation of organic substrates in which water is selectively removed from the reaction mixture during the reaction by means of membranes.

10 The only single oxygen oxidation ( $^1\text{O}_2$  oxidation) which is currently carried out industrially is the photochemical  $^1\text{O}_2$  oxidation in which the  $^1\text{O}_2$  is generated by a photochemical route. The disadvantage of this process results from the high cost of the photochemical equipment required, and by a limited service life. The  
15 required lamps degenerate relatively rapidly during the oxidation as a result of soiling of the glass surface. In addition, this process is not suitable for coloured substrates. The process is actually suitable only for fine chemicals which are prepared on a relatively small  
20 scale. (La Chimica e l'Industria, 1982, Vol. 64, page 156).

For this reason, attempts have been made to find other process variants for the  $^1\text{O}_2$  oxidation in which  $^1\text{O}_2$  is generated chemically instead of photochemically.

25 J. Am. Chem. Soc., 1968, 90, 975 describes, for example, the classical "dark"  $^1\text{O}_2$  oxidation in which  $^1\text{O}_2$  is generated not photochemically, but chemically. In this process, hydrophobic substrates are oxidized by  
30 means of a hypochlorite/ $\text{H}_2\text{O}_2$  system in a solvent mixture of water and organic solvent. Due to the secondary reactions between hypochlorite and substrate or solvent, the potential use of this process is somewhat limited. In addition, this process is not suitable for  
35 the industrial scale since addition of the hypochlorite onto  $\text{H}_2\text{O}_2$  results in the organic medium, and a large excess of  $\text{H}_2\text{O}_2$  is required to suppress the secondary reaction of substrate with hypochlorite. An additional

disadvantage arises as the result of the formation of stoichiometric amounts of salt.

5 A variant of the dark  $^1\text{O}_2$  oxidation which is not based on hypochlorite and thus should partly avoid the above disadvantages, is known, for example, from J. Org. Chem., 1989, 54, 726 or J. Mol. Cat., 1997, 117, 439, according to which some water-soluble organic substrates are oxidized with  $^1\text{O}_2$  and a molybdate catalyst in water as solvent.

15 The disadvantage of the dark  $^1\text{O}_2$  oxidation known hitherto which is carried out in water or a mixture of water and organic solvent is, however, as described, for example, in J. Am. Chem. Soc. 1997, 119, p. 5286, that the majority of the  $^1\text{O}_2$  is lost as a result of quenching by the water molecules, meaning that a large excess of  $^1\text{O}_2$  is required in order to achieve acceptable conversions.

20 Since  $\text{H}_2\text{O}_2$  is usually obtainable as an up to 30 or 35% strength aqueous solution and, additionally, water also arises during the formation of  $^1\text{O}_2$ , reactions in which the singlet oxygen used as oxidizing agent is obtained in situ from  $^1\text{O}_2$  additionally suffer from additional dilution of the reaction medium with water. This also leads to reaction volumes being lost in the case of batch reactions, as a result of which the space-time yield is likewise reduced.

30 A further disadvantage of dark  $^1\text{O}_2$  oxidation in water or in water/solvent mixtures consists in the fact that, in the case of some organic substrates, in particular in the case of those with a relatively high molecular weight, demixing or phase separation arises when the water content of the reaction medium is high, which has a very negative effect on the yield.

Accordingly, it was an object of the present invention to find an improved method of the dark  $^1\text{O}_2$  oxidation which can be carried out simply, cost-effectively and in an environmentally friendly manner on the industrial scale, with the disadvantages which arise as a result of the presence of water being overcome.

Unexpectedly, it has now been found that the dark  $^1\text{O}_2$  oxidation can be carried out in an extremely efficient manner with a high yield in water or in water/solvent mixtures if water is selectively removed from the reaction mixture during the reaction by means of membranes.

Accordingly, the present invention provides an improved process for the oxidation of organic substrates by means of  $^1\text{O}_2$ , which is characterized in that 3-90% strength  $\text{H}_2\text{O}_2$  is added to organic substrates which are soluble in water or in organic solvents miscible with water and which react with  $^1\text{O}_2$ , in a water-miscible organic solvent, in water or in a mixture of water and water-miscible organic solvent in the presence of a heterogeneous or homogeneous catalyst, whereupon, following the catalytic decomposition of  $\text{H}_2\text{O}_2$  to give water and  $^1\text{O}_2$ , the oxidation of the substrates to give the corresponding oxidation product takes place, where, during the reaction, water is selectively removed from the reaction mixture by means of membranes.

The process according to the invention is suitable for the oxidation of organic substrates which are water-soluble or soluble in water-miscible organic solvent and which react with  $^1\text{O}_2$ .

Suitable substrates are described, for example, in WO 00/64842 and WO 00/61524. Excluded are those substrates which are highly hydrophobic such as, for example, rubrene, and those which are insoluble in water or in a water-miscible organic solvent.

Accordingly, the following compounds may be used as substrates: olefins which contain one or more, i.e. up to 10, preferably up to 6, particularly preferably up to 4, C=C double bonds; electron-rich aromatics, such as C<sub>6</sub>-C<sub>30</sub>-, preferably up to C<sub>20</sub>-, particularly preferably up to C<sub>15</sub>-aromatics, such as, for example, phenols, polyalkylbenzenes, polyalkoxybenzenes, etc.; polycyclic aromatics with 2 to 8, preferably up to 4, particularly preferably up to 3, aromatic rings; sulfides, such as, for example, alkyl sulfides, alkenyl sulfides, aryl sulfides which are either mono- or disubstituted on the sulfur atom, and heterocycles with one or more O, N or S atoms in the ring, such as, for example, C<sub>4</sub>-C<sub>30</sub>-, preferably up to C<sub>20</sub>-, particularly preferably up to C<sub>15</sub>-heterocycles, such as, for example, furans, pyrroles, thiophenes, thiazoles, pyridines, isobenzofurans, quinolines etc.

The substrates can here have one or more substituents, such as halogen, (F, Cl, Br, I), cyanide, carbonyl groups, hydroxyl groups, C<sub>1</sub>-C<sub>20</sub>, preferably up to C<sub>10</sub>, particularly preferably up to C<sub>6</sub>, alkoxy groups, C<sub>1</sub>-C<sub>20</sub>-, preferably up to C<sub>10</sub>-, particularly preferably up to C<sub>6</sub>-alkyl groups, C<sub>6</sub>-C<sub>30</sub>, preferably up to C<sub>20</sub>, particularly preferably up to C<sub>10</sub>, aryl groups, C<sub>2</sub>-C<sub>20</sub>, preferably up to C<sub>10</sub>, particularly preferably up to C<sub>6</sub>, alkenyl groups, C<sub>2</sub>-C<sub>20</sub>, preferably up to C<sub>10</sub>, particularly preferably up to C<sub>6</sub>, alkynyl groups, carboxylic acid groups, ester groups, amide groups, amino groups, nitro groups, silyl groups, silyloxy groups, sulfone groups, sulfoxide groups.

In addition, the substrates can be substituted by one or more NR<sup>1</sup>R<sup>2</sup> radicals in which R<sup>1</sup> or R<sup>2</sup> may be identical or different and are H; C<sub>1</sub>-C<sub>20</sub>, preferably up to C<sub>10</sub>, particularly preferably up to C<sub>6</sub>, alkyl; formyl; C<sub>2</sub>-C<sub>20</sub>, preferably up to C<sub>10</sub>, particularly preferably up to C<sub>6</sub>, acyl; C<sub>7</sub>-C<sub>30</sub>, preferably up to C<sub>20</sub>, particularly preferably up to C<sub>10</sub>, benzoyl, where R<sup>1</sup> and R<sup>2</sup> can also together form a ring, such as, for example, in a phthalimido group.

Examples of particularly suitable substrates are: 1,3-butadiene; 2,3-dimethylbutene;  $\Delta^{9,10}$ -octalin, 2,3-dimethyl-1,3-butadiene; 2,4-hexadiene; 1,3-cyclohexadienes, 4-methyl-3-penten-2-ol, 3,4-dimethyl-3-penten-2-ol, 3-(4-methyl-1-naphthyl)propionic acid, 3,3'-(naphthalene-1,4-diyl)dipropionic acid, 1-trimethylsilylcyclohexene; (E)-2-methylcrotonic acid, 2,3-dimethyl-2-butenyl para-tolyl sulfone; 2,3-dimethyl-2-butenyl para-tolyl sulfoxide; N-cyclohexenylmorpholine; 2-methyl-2-norbornene; terpinolene;  $\alpha$ -pinene;  $\beta$ -pinene;  $\beta$ -citronellol; ocimene; citronellol; geraniol; farnesol; terpinene; limonene; trans-2,3-dimethylacrylic acid,  $\alpha$ -terpinene; isoprene; cyclopentadiene; 1,4-diphenylbutadiene; 2-ethoxybutadiene; 1,1'-dicyclohexenyl; cholesterol; ergosterol acetate; 5-chloro-1,3-cyclohexadiene; 3-methyl-2-buten-1-ol; 2-phthalimido-4-methyl-3-penten-2-ol, phenol, 1,2,4-trimethoxybenzene, 2,3,6-trimethylphenol, 2,4,6-trimethylphenol, 1,4-dimethylnaphthalene, furan, furfuryl alcohol, furfural, 2,5-dimethylfuran, isobenzofuran, dibenzyl sulfide, (2-methyl-5-tert-butyl)phenyl sulfide, diphenyl sulfide, etc.

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The substrates can also be used in the form of a salt, for example in the form of the Na or K salt or in the form of the tetra-C<sub>1</sub>-C<sub>6</sub>-alkylammonium salt.

30 The corresponding oxidation product is obtained from the substrates by the oxidation according to the invention. Alkenes, (polycyclic) aromatics or heteroaromatics give, in particular, hydroperoxides or peroxides, which can further react under the reaction  
35 conditions to give alcohols, epoxides, acetals or carbonyl compounds, such as ketones, aldehydes, carboxylic acids or esters, if the hydroperoxide or the peroxide is not stable.

The oxidation according to the invention takes place in a water-miscible organic solvent or in water or in a mixture of water and a water-miscible organic solvent.

Suitable water-miscible solvents are C<sub>1</sub>-C<sub>8</sub> alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol; ethylene glycol, propylene glycol, formamide, N-methylformamide, dimethylformamide (DMF), sulfolane, dioxane, THF and 1,2-dimethoxyethane.

Preference is given to using methanol, ethanol, propanol, isopropanol, dioxane, DMF and THF, particular preference to using methanol, ethanol or THF as water-miscible solvent.

A metal which is suitable for <sup>1</sup>O<sub>2</sub> oxidations and is described, for example, in WO 00/64842 and WO 00/61524, J. Am. Chem. Soc., 1985, 107, 5844, Chem. Eur. J. (2001) 7(12), p. 2547-2556 or in Membrane Lipid Oxid. Vol. II, 1991, 65, is added as heterogeneous or homogeneous inorganic catalyst to the solvent-substrate mixture.

Preference is given to using catalysts based on molybdenum, tungsten, scandium, vanadium, titanium, zirconium, praseodymium, neodymium, samarium, europium, terbium, dysprosium, holmium, erbium, ytterbium, lanthanum, cerium or gadolinium, and also the so-called pseudo-lanthanides scandium and yttrium and lutetium. Particularly preference is given to molybdenum and lanthanum catalysts.

In this connection, the metal can be in forms customary for <sup>1</sup>O<sub>2</sub> oxidations, for example as the oxide, oxo complex, nitrate, carboxylate, hydroxide, layered double hydroxide (LDH), carbonate, chloride, fluoride, sulfate, tetrafluoroborate, etc. A hydroxide, for example NaOH, KOH, etc., can optionally be added to homogeneous, soluble forms of the catalyst to give a heterogeneous, active catalyst.

The amount of catalyst used depends on the substrate used and is between 1 and 50 mol%, preferably between 5 and 25 mol%.

- 5 In some instances, it may be advantageous, for better activation of the catalyst, if customary basic or acidic additives are added to the reaction mixture.

10 3-90% strength, preferably 30-60% strength,  $\text{H}_2\text{O}_2$  is then added. Preferably,  $\text{H}_2\text{O}_2$  is added slowly or in portions to the reaction mixture of solvent, substrate and catalyst, during which the reaction mixture is stirred. It is also possible to firstly add only some of the  $\text{H}_2\text{O}_2$ , then a hydroxide, such as, for example, NaOH, KOH  
15 etc., and then the remaining amount of  $\text{H}_2\text{O}_2$ .

The consumption of  $\text{H}_2\text{O}_2$  in the process according to the invention is dependent on the substrate used. For reactive substrates, 2 to 3 equivalents of  $\text{H}_2\text{O}_2$  are  
20 preferably required, whereas less reactive substrates are preferably reacted with 3 to 10 equivalents of  $\text{H}_2\text{O}_2$ .

The reaction temperature is between 0 and 50°C, preferably between 15 and 35°C.  
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The pH of the reaction mixture depends on the chosen substrate and the chosen catalyst and can be between 0 and 14, preferably between 4 and 14. The pH of the reaction mixture can, if necessary, be adjusted as  
30 required using customary basic or acidic additives.

According to the invention, in the present process, water is selectively removed by means of membranes. In this connection, water which is optionally used as  
35 solvent and water which is introduced by the 2-90% strength  $\text{H}_2\text{O}_2$  solution and which is formed during the catalysed disproportionation of  $\text{H}_2\text{O}_2$ , and optionally present water-miscible organic solvent is removed from the reaction mixture simultaneously by a membrane unit,

whereupon distillative separation of the water from the organic solvent then optionally takes place. The organic solvent is then reintroduced into the reactor. The process scheme is shown in Figure 1 and shows a

5 reactor (1) in which the solvent or solvent mixture, the substrate and the catalyst are initially introduced and into which  $H_2O_2$  is then introduced via line (2). Via a pump (3), the reaction mixture passes into the membrane unit (4). In the membrane unit (4), water

10 (permeate) is then separated off through a suitable membrane, the catalyst (in the case of a homogeneous catalyst), the still unreacted substrate and product already formed being retained (retentate) and immediately reintroduced into the reactor.

15 Depending on the membrane chosen, the optionally used water-miscible organic solvent is either likewise retained, as is the case, for example, for MeOH for the use of inorganic membranes, or else is separated off with the water.

20 For the case that the organic solvent is separated off with the water from the reaction mixture, distillative separation (distillation column (5)) of water and water-miscible solvent then takes place, whereupon the solvent is returned to the reactor (line (6)) and the

25 separated-off water is discarded.

In the process according to the invention, instead of one membrane unit, it is also possible to use two or more membrane units. If two membrane units are used,

30 the permeate of the first unit is passed to the second membrane unit, and the retentate of the first membrane unit is returned, as described above, to the reactor. The retentate of the second unit is then likewise returned to the reactor, while the permeate of the

35 second unit is worked up as described above (removal of the solvent by distillation) or, if the permeate comprises only water, is discarded.



For the process according to the invention, both organic and also inorganic membranes are suitable.

Suitable organic membranes are membranes for reverse osmosis (R.O.) which consist, for example, of polyvinyl alcohol, polyamide or polysulfone or cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose diacetate/cellulose triacetate (CDA/CTA), cellulose nitrate, polypropylene, polyimide, sulfonated polysulfones, polyethersulfones, polyacrylonitrile, polyimide/polyetherimide, polyvinylidene fluoride, aramid or polypiperazine or mixtures thereof. Preference is given to those membranes which retain molecules with a molecular weight between 50 and 200 Da (g/mol), particularly preferably between 50 and 100 Da.

Further suitable organic membranes are membranes for nanofiltration whose active separation layer comprises, for example, polyvinyl alcohol, polypropylene, polysulfone, polyether-sulfone, polyacrylonitrile, polyimide/polyether-imide, polyvinylidene fluoride, polyamide, polypiperazine, cellulose acetate, cellulose nitrate, aramide, cellulose diacetate, cellulose triacetate, etc. or mixtures thereof. Preference is given to those nanofiltration membranes which retain molecules with a molecular weight between 50 and 400 Da (g/mol), particularly preferably between 50 and 200 Da.

As organic membranes, preference is given to using R.O. membranes, which are in fact suitable for all suspended and dissolved materials since these are all retained.

Commercially available R.O. membranes are, for example, Toray SU810 (Toray, based on polyamide), PCI ACF99 (PCI, based on polyamide), DESAL SC (Osmonics-Desalination Systems, based on cellulose acetate), Pall Rochem 05757, SW 30 HR (Film Tec-DOW, based on polyamide), Trisep X-20 (Trisep, based on ACM/cellulose

acetate), NTR 759 (Nitto Denko; based on polyvinyl alcohol/polyamide), NTR 729 (Nitto Denko; based on polyvinyl alcohol); Pervap 1510 (Deutsche Carbone AG), CMC-CE01 (Celfa, based on polyvinyl alcohol) etc.

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Commercially available N.F. membranes are, for example, Desal 5K (Osmonics-Desalination Systems; based on polyamide), Koch MPF60 (Koch-Membrane Products), NF200 (Filmtec DOW; based on polypiperazinamide), NF CA30 (Nadir; based on cellulose acetate) etc.

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In addition, suitable organic membranes are also organic pervaporation membranes whose active separation layer comprises polydimethylsiloxanes, poly(1-trimethylsilyl-1-propyne), polyurethanes, polybutadiene, polyether block polyamides, silicone polycarbonates, styrene-butadiene rubber, nitrile-butadiene rubber, ethene-propene terpolymer, polyvinyl alcohol, polyamide, polysulfone, cellulose acetate, aramid, cellulose diacetate, cellulose triacetate, polypiperazine etc. or mixtures thereof.

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Organic pervaporation membranes are characterized in that they effectively separate water from molecules which are larger than 4.5 Å. They are preferably used for separating off molecules greater than 5 Å in size.

The inorganic or ceramic membranes used are preferably membranes for the pervaporation technique. These are membranes which consist, for example, of an active layer based on aluminium, titanium dioxide, silica, boron oxide, magnesium, zirconium, clay etc. or mixtures thereof, on a suitable carrier, such as, for example, a gamma-Al<sub>2</sub>O<sub>3</sub> carrier.

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Commercially available pervaporation membranes are, for example, Sulzer Pervap SMS (Sulzer, silica membrane system).

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These inorganic pervaporation membranes are also characterized by the fact that they effectively

separate water from molecules which are larger than 4.5 Å. They are preferably used for separating off molecules greater than 5 Å in size.

- 5 Also suitable are ceramic nanofiltration membranes based on aluminium, boron oxide, magnesium, zirconium, TiO<sub>2</sub>, SiO<sub>2</sub>, clay etc. or mixtures thereof, for example from HITA (Hermsdorfer Institut für Technische Keramik [Hermsdorf Institute of Technical Ceramics]), and TAMI  
10 (Tami Industries) etc., and zeolite membranes based on aluminium, boron oxide, magnesium, zirconium, TiO<sub>2</sub>, SiO<sub>2</sub>, clay etc. or mixtures thereof.

15 Preference is given to using ceramic membranes for the process according to the invention.

The most important parameters for suitable membranes here are:

- capacity: permeate flow, kg/m<sup>2</sup>.h.bar
- 20 - selectivity: retention or separation factor,
- mechanical stability: abrasion, temperature
- chemical stability: towards solvents and oxidising agents

- 25 Suitable membranes should have a retention factor for substrate and product of at least 85%, preferably of at least 95%, in order to keep substrate and product losses as low as possible.

If two membrane units are used, then membranes with a  
30 relatively low retention factor of at least 80%, preferably of at least 90%, can be used.

The choice of a suitable membrane is made depending on the chosen reaction medium, substrate, product and  
35 catalyst.

Preferably, suitable membranes are ascertained in preliminary experiments in which the stability in the reaction medium, the retention factor with regard to

substrate and product, the capacity (permeate flow) etc. are investigated.

5 The process according to the invention avoids the  
reaction mixture becoming increasingly diluted by the  
water introduced with the hydrogen peroxide (through  
the use of a 3-90% strength solution and by  
disproportionation to water and  $^1\text{O}_2$ ). As a result,  
losses in yield in the case of the batch procedure and  
10 negative influences on the solubility (demixing etc.)  
and the efficiency of the  $^1\text{O}_2$  are prevented. In  
addition, negative influences of water on the  
stereoselectivity of the reaction are prevented.  
As a result of the water removal according to the  
15 invention, it is accordingly possible to increase the  
yields in the case of the batch procedure by up to more  
than 200%, and to increase the stereoselectivity of the  
reaction.

Comparative Experiment: without water removal

A mixture of methanol, 2-methylcrotonic acid and  $\text{Na}_2\text{MoO}_4$  catalyst was initially introduced into a reactor. A 30% strength by weight  $\text{H}_2\text{O}_2$  solution was then added. The batch volume increased as a result of the water which formed during the catalysed disproportionation of  $\text{H}_2\text{O}_2$ , and by the volume of water in the 30% strength by weight  $\text{H}_2\text{O}_2$  solution. The total volume at the end of the batch experiment determines the maximum initial charging of the reactor or the batch yield at the end of the reaction.

Table 1 gives the reaction parameters

$\text{H}_2\text{O}_2$ /substrate mol/mol	% water at end of batch % by wt.	[substrate] mol/l	Batch yield kg
2	5.0	0.22	196
2	30.0	1.93	1333
2	18.9	1	795
2	49.5	5.1	2431
10	5.0	0.04	39
10	30.0	0.36	251
10	53.9	1	481
10	84.9	5	810

**Example 1:** Water removal using a membrane unit

A mixture of methanol, substrate and  $\text{Na}_2\text{MoO}_4$  catalyst was initially introduced into a reactor. A 30% strength by weight  $\text{H}_2\text{O}_2$  solution was then added. The batch volume increased by the water which formed during the catalysed disproportionation of  $\text{H}_2\text{O}_2$ , and by the volume of water in the 30% strength by weight  $\text{H}_2\text{O}_2$  solution.

After the previously determined total content of water had been reached, the membrane unit (Celfa) was set in

operation in order to remove further water which was added and which formed. Likewise removed methanol was completely recovered by distillative separation and returned to the reactor.

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Table 2: Batch yield for a readily oxidizable substrate, such as, for example,  $\beta$ -citronellol with an  $H_2O_2$ /substrate molar ratio = 2;

Retention	Water content % by wt.	Batch yield kg	% increase compared with Comp. Ex.	Yield %
90	5	609	211	64
95	5	759	287	80
99	5	908	363	96
100	5	950	385	100

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Table 3: Batch yield for a substrate which is difficult to oxidize, such as, for example, tiglic acid with an  $H_2O_2$ /substrate molar ratio = 10;

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Retention	Water content % by wt.	Batch yield kg	% increase compared with Comp. Ex.	Yield %
90	5	91	133	10
95	5	291	646	31
99	5	748	1818	78
100	5	950	2336	100
90	30	677	170	71
95	30	801	219	84
99	30	917.8	266	96.6
100	30	950	278	100

**Example 2:** Water removal with two membrane units

The experiment was carried out analogously to Example 1, although two membrane units were used to remove the water.

Table 4: Batch yield for a readily oxidizable substrate with an  $H_2O_2$ /substrate molar ratio = 2;

Retention	Water content % by wt.	Batch yield kg	% increase compared with Comp. Ex.	Yield %
90	5	898	358	95
95	5	937	378	98.6
99	5	949.5	384	99.94
100	5	950	385	100

Table 5: Batch yield for a substrate which is difficult to oxidize with an  $H_2O_2$  substrate molar ratio - 10;

Retention	Water content % by wt.	Batch yield kg	% increase compared with Comp. Ex.	Yield %
90	5	707	1713	75
95	5	881	2159	93
99	5	947	2328	99.69
100	5	950	2336	100
90	30	912	262	96
95	30	940	275	98
99	30	949.6	278	99.96
100	30	950	278	100

**Example 3:**

It was investigated whether organic R.O. membranes are suitable for the removal of a water/methanol mixture

coupled with simultaneously high retention of substrate and product:

5 In an experimental plant according to Figure 1, a test solution of 7% by weight of Na tiglate, 5% by weight of water and 88% by weight of methanol was pumped at 25°C and a pressure difference of 30 bar at the membrane from the reactor using a pump through the membrane unit (R.O. membrane, type NTR 759), and the retention, and  
10 also the flow, were determined.

Beforehand, the membrane was stored for 5 days at room temperature and atmospheric pressure for stabilisation in 5% by weight of water/methanol.

15 Result: 96% retention of Na tiglate, 2 kg/m<sup>2</sup>/h flow

**Example 4:**

It was investigated whether organic R.O. membranes are stable under singlet oxygen oxidation conditions:

20 In an experimental plant according to Figure 1, a test solution of 7% by weight of Na tiglate, 5% by weight of water and 88% by weight of methanol was pumped at 25°C and a pressure difference of 30 bar at the membrane by means of a pump from the reactor through the membrane  
25 unit (R.O. membrane, type NTR 759), and the retention, and also the flow were determined.

Beforehand, the membrane was exposed for 5 days to singlet oxygen oxidation conditions: 5% by weight of water/methanol, pH about 10, 0.02M Na<sub>2</sub>MoO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> addition  
30 at an H<sub>2</sub>O<sub>2</sub>/catalyst molar ratio of 3, room temperature, atmospheric pressure; the solution was renewed 6 times per day.

Result: 85% retention of Na tiglate, 13-16 kg/m<sup>2</sup>/h flow  
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**Example 5:**

It was investigated whether a ceramic pervaporation membrane is suitable for the removal of a



water/methanol mixture with simultaneously high retention of substrate and product:

5 In an experimental plant according to Figure 1, a test  
solution of 7% by weight of Na tiglate, 5% by weight of  
water and 88% by weight of methanol was pumped at 25°C  
and a pressure difference of 7 bar at the membrane by  
means of a pump from the reactor through the membrane  
unit (Sulzer Pervap SMS), and the retention, and also  
10 the flow were determined.

Result: 100% retention of Na tiglate, 0.1 kg/m<sup>2</sup>/h flow;  
water/methanol selectivity = 6